HEAVY METAL GEOCHEMISTRY IN THE SEDIMENTS OF A BRAZILIAN MANGROVE

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ABSTRACT

The purpose of this study is to observe the effects of seasonal redoxcline migration on sedimentary iron and associated heavy metal in mangrove sediments located at the estuary of the Paraíba do Sul River . The site can be considered a natural environment, as a result of the absence of large metal pollution sources in the lower Paraíba do Sul River basin, and marine sediment dilution. The main factor affecting the total heavy metal contents was spatial heterogeneity, and no seasonal pattern was observed.

INTRODUCTION

Reactive sedimentary iron presents a relevant function in marine sediments, related with organic matter decomposition and pyrite formation, as well as with phosphate and trace metal sedimentary pools (Kostka & Luther, 1994). In temperate salt marsh environments it has been described a seasonal dinamic cicle of sedimentary iron (Giblin & Howarth, 1984; Kostka & Luther, 1995). Redox sedimentary conditions can be affect by several factors, including seasonal redoxcline migration induced by variations in the fluvial discharge. The Paraíba do Sul River discharge varies from 400 $m^3.s^{-1}$ at dry season to 2,500 $m^3.s^{-1}$ in the wet season, and the inundation of marginal areas presents a seasonal pattern (Salomão et al., 1999). The estuary is located at the north of Rio de Janeiro State, Brazil, ($21^0$36’00”S e $41^0$03’00’’W) and is the object of several studies related with heavy metal contamination (Molisani et al., 1999; Salomão et al., 1999). In this study we observed the effect of seasonal inundation pattern on total sedimentary metal contents in a mangrove ecosystem.

METHODS

We realized two sampling field campaigns in the dry season (August and September, 1998) and two in the wet season (January and February, 1999). For each campaign we colected sediment cores, sectioned at each 5 cm in inert environment. Porewater samples were obtained with *in situ* devices previously described (Aragon et al. 1999) and analyzed for physical-chemical variables and ferrous and ferric dissolved contents. The sediment samples were then freeze-dried, and subsamples were used for the determination of reactive iron and trace metals using HCl 0.5 M for 1 hour (Kostka & Luther III, 1994). Total metal contents were determined with concentrated HNO_3 and HF in Teflon bombs at 100°C (Molisani, 1999). The determination of of Fe, Mn, Ni, Zn, Cu, Cr and Cd was proceeded by ICP/EAS. Variation coefficient (%) for triplicate analytical results was 5.2 (Fe), 6.1 (Mn), 4.8 (Zn), 4.6 (Cr), 4.2 (Cu) and 10 (Pb).

RESULTS AND DISCUSSION

Porewater samples collected in dry season showed acidification related with more oxidant conditions indicated by de E_H . The highest anoxic conditions observed at the January campaign were accompanied by the highest porewater dissolved ferrous iron contents, suggesting an intense dynamics for the reactive iron pool (Silva et al., 1999). On the other hand, the total sedimentary metal contents presented no seasonal pattern. The spatial heterogeneity, conditioned by physical, chemical and biological factors as root distribution and crab activity dominated the total metal contents pattern for most analyzed metals (Figure 1). Range of variation were: Fe 2.5 – 7.6; Al 1.6 – 12.0; Mn 56 – 127; Zn 36 – 105; Pb 9 – 24; Ni <3 – 36, Cu 17 – 35 and Cr 42 – 78; Cd <1 (Fe and Al in % ; others in µg/g).

The contents of iron, manganese, zinc, cooper and chromium are lower than those presented in Molisani et al. (1999) for the fraction <63µm of bottom sediments in a tidal creek at the same location, as a consequence of sand particles dilution. The results are compatible with the low contamination pattern previously reported for sediments of the Paraíba do Sul River Estuary, and is attributed to the absence of large metal pollution sources in the lower fluvial basin (Molisani et al., 1999) as well as dilution promoted by marine sediments.

We used in this study total sediment for the analysis of total and reactive metal contents, because for toxicological considerations it is the most realistic, and it is the same procedure that we are using for pyrite contents determination by sequential extractions (Huerta Diaz & Morse, 1990). We understand that our results are strongly affected by the grain size heterogeneity in the sediments, but when we analyze the percentage of reactive metal related with total metal contents this effect is minimized.

The percentage of reactive metal related with total metal contents is less affected by grain size effects, and the results are presented in Table 1. Pyrite iron and associated heavy metal are not included in the reactive phase.

Table 1. Percentage of total metal contents in the reactive phase (n = 4).

	Mean percentage of total metal contents in the reactive phase (%)					
Depth (cm)	**Fe**	**Al**	**Mn**	**Cu**	**Ni**	**Cr**
0 - 5	22	4	33	15	1	1
20 - 25	6	4	12	2	0	0
50 - 55	1	5	15	1	0	0

Our results evidenced a greater percentage of reactive Fe, Mn and Cu in the superficial sediments (0 to 5 cm depth) probably related with organic matter contents. As antropogenic contamination is not relevant in the studied site, the vertical pattern can be attributed to diagenetic processes.

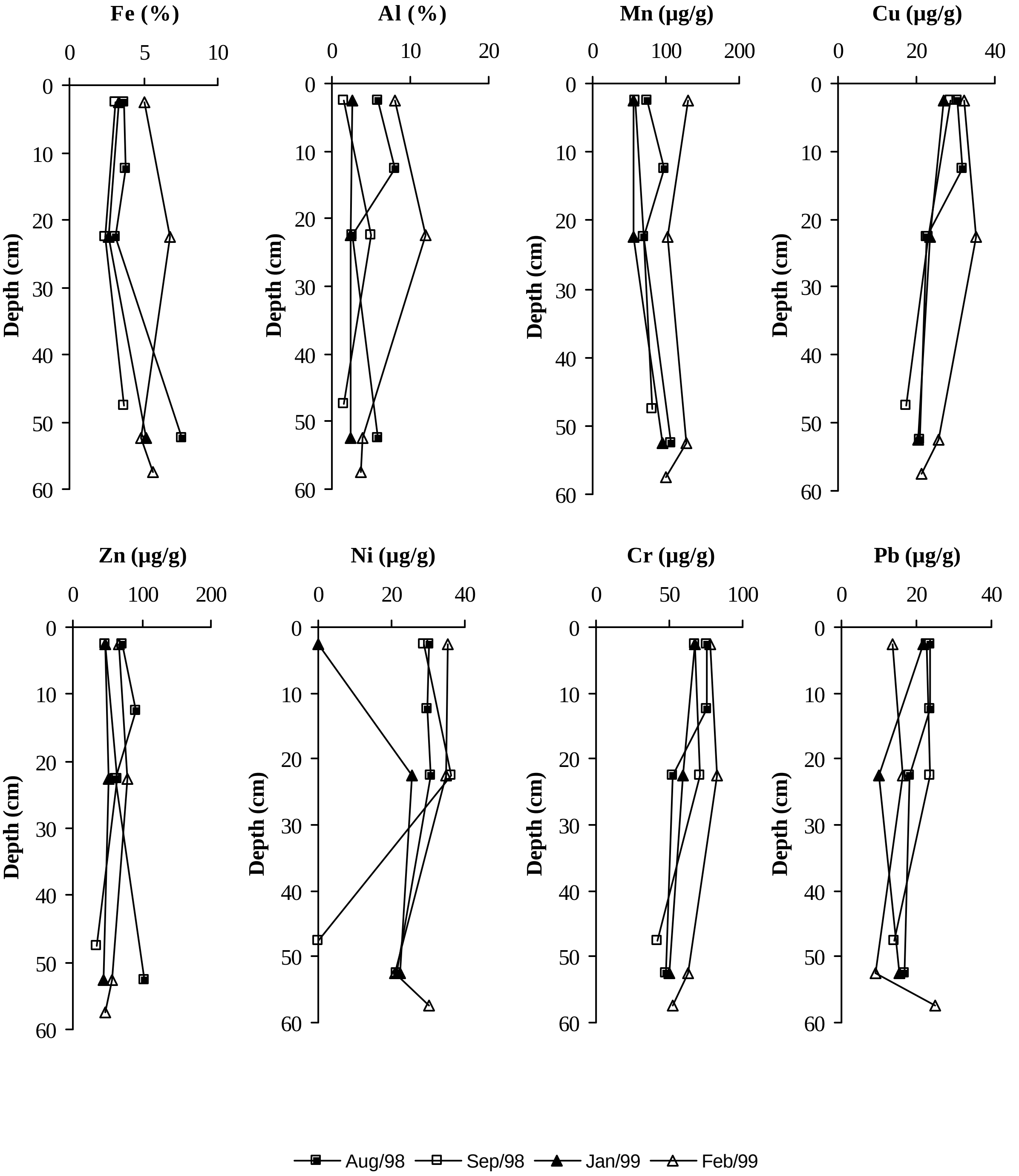
Fe (%)
0
5
10
Al (%)
0
10
20
Mn (µg/g)
0
100
200
Cu (µg/g)
0
20
40
Zn (µg/g)
0
100
200
Ni (µg/g)
0
20
40
Cr (µg/g)
0
50
100
Pb (µg/g)
0
20
40
Depth (cm)
0
10
20
30
40
50
60
Aug/98
Sep/98
Jan/99
Feb/99

Figure 1. Total heavy metal contents in the sediments, iron and aluminum (%), Mn, Cu, Zn, Ni, Cr and Pb (µg/g) in cores obtained during dry (August and September) and wet (January and February) seasons.

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